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ISOTOPICALLY ANOMALOUS SILVER IN THE SANTA CLARA AND PIÑON IRON METEORITES

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Abstract. The isotopic composition and concentration of Ag and the concentration of Pd have been determined in the Santa Clara and Piñon iron meteorites. It is shown that these meteorites contain isotopically anomalous Ag with an excess of ^{107}Ag relative to normal Ag, confirming earlier findings. Using an improved procedure for cleaning the sample surface from terrestrial Ag, a new concentration of 1-4x10^{11} atoms of ^{109}Ag/g meteorite is established which is an order of magnitude below the levels found earlier. As a result ratios of ^{107}Ag/^{109}Ag were found which are enriched in ^{107}Ag by 60% to 160%. The existence of an excess ^{107}Ag in these two meteorites, which have high ^{108}Pd/^{109}Ag ratios of ~ 7x10^4, is established. These findings are consistent with the *in situ* decay of extinct ^{107}Pd ($\tau_{1/2}$ = 6.5x10^{6}y) produced by a late nucleosynthetic event shortly before solar system formation; however, production of Ag isotopes by reaction of cosmic ray secondaries with the Pd isotopes in the meteorites cannot be excluded.

Introduction. We present evidence for very large anomalies in the isotopic composition of Ag extracted from the Santa Clara and Piñon iron meteorites and establish that the ^{109}Ag concentration in these meteorites is about a factor of ten less than reported previously. Isotopically anomalous Ag has so far only been found in meteorites with very high Pd/Ag ratios. *Kelly and Wasserburg* [1978, 1979; hereafter KW1 and KW2 or collectively as KW] discovered ^{107}Ag/^{109}Ag ratios greater than the terrestrial value by 4 to 7% in the Santa Clara iron meteorite. These workers also reported that the meteorite Piñon showed an excess in ^{107}Ag/^{109}Ag of 4% (oral presentation [KW2]). They concluded that the ^{107}Ag* (* ≡ excess) is most plausibly explained by the decay of extinct ^{107}Pd ($\tau_{1/2}$ = 6.5x10^{6}y) which was produced with ^{26}Al ($\tau_{1/2}$ = 7.3x10^{5}y) in a late stage nucleosynthetic event and injected into the early solar system together with ^{26}Al shortly before or during the formation of the meteorite parent bodies. This implies that late stage nucleosynthesis, condensation of refractory elements, and the earliest planetary differentiation occurred within a few half-lives of ^{107}Pd during the formation of the solar system. This discovery was made possible by the development of analytical capabilities which permit determination of the ^{107}Ag/ ^{109}Ag ratio on 10^{11} atoms of Ag with a precision of 1% [*Kelly, Tera, and Wasserburg*, 1978; hereafter KTW]. The primary goal of this work was to test and extend the evidence for the presence of ^{107}Ag* and to clarify the variations in the Ag concentration reported by KW. KW found that the concentration of Pd and of ^{107}Ag* was constant in different samples of Santa Clara. However, a component of normal Ag was present which exhibited substantial variation in concentration among different pieces of the same meteorite. If this variable normal Ag component were truly indigenous to the meteorite, as a result of chemical fractionation into different mineral phases during the formation of the meteorite, then this would constitute strong evidence that the ^{107}Ag* was built up due to *in situ* decay of ^{107}Pd subsequent to the Pd-Ag fractionation. On the other hand, if the fluctuations in the amount of the normal Ag component were due to terrestrial contamination, this argument may not apply. Consequently we have made considerable efforts to eliminate contributions from terrestrial Ag to the limits of our technical capability.

Materials. The acids described in the procedures below were produced by the National Bureau of Standards (sub-boiling distillation). Dilutions from 11-12 N HCl and 14 N HNO_3 were made using our quadruple distilled water (SiO_2 glass). Typical concentrations of Ag in these reagents were 6x10^8, 6x10^8, and 3x10^8 atoms of Ag/g of reagent, respectively. Ion exchange resins from Bio-Rad (100-200 mesh), types AG 1-x8 (Cl^--form), and 50W-x8 (H^+-form) were used. Micro-columns for the ion exchange procedure were made of suprasil quartz. All other SiO_2 ware was of normal fused quartz. All samples were handled in Nalge FEP-Teflon beakers.

Dissolution of meteorite samples. Sawed pieces of the meteorites were first cleaned from terrestrial Ag as follows. The outer surface was treated with analytical grade CCl_4 and methanol and then dissolved in 3-5 steps with hot aqua regia. Each step removed approximately 0.8 g of material from the surface. The samples were constantly turned during this step with quartz chop sticks in the Swiss manner. After each dissolution stage the residual metal piece was cleaned with conc. HCl from adhering FeOOH and thoroughly rinsed with H_2O. An aliquot of the solution comprising all of the meteorite that was dissolved away in each "etching" step was then passed through the chemical separation procedure for Ag and Pd and analyzed in the mass spectrometer. The metal was dried in filtered N_2 in a Teflon pot with a quartz cover under an infrared lamp [see *Sanz and Wasserburg*, 1969]. The metal was then weighed and the change in weight determined the amount removed by etching. All samples were examined under a microscope for signs of preferential dissolution of phases and for penetration of acid into the interior. No indications for preferential leaching below the exposed surface could be seen except for black nodules, 0.1-2 mm in size, most likely daubreelite, which were more rapidly dissolved than the surrounding metal matrix. A piece of Piñon was examined with a scanning electron microscope before and after the chemical treatment of the surface. The original surface showed 10-200 μm deep rills produced by the saw. After chemically removing a ~ 450 μm thick surface layer, the saw marks had disappeared and the metal matrix showed an etching pattern ~ 1–5 μm in size due to preferential dissolution of kamacite compared to taenite. With this exception, the metal matrix looked dense and smooth. Schreibersite nodules (size 5-500 μm) stood in high positive relief (~ 100 μm) indicating that they dissolved more slowly than the surrounding metal. Most schreibersite grains were found in spindle shaped cavities (50-500 μm). These were probably filled originally with pure kamacite [see *Buchwald*, 1975] which was preferentially removed during etching. We believe that the alteration of the bulk sample composition due to the surface cleaning procedure and etching steps is small compared to the sample size and that the metal removed in each step represents successive layers of metal which are concentric with the central piece.

Separation of Ag from the meteoritic metal. Based on the experience gained from the microchemical separation of Pb [*Tera and Wasserburg*, 1975], a separation procedure for Ag has gradually been developed by KTW and KW. The procedure described below is a summary of the methods used by us and follows KTW+KW. After dissolution, 1-2 g meteoritic FeNi in 50 ml 0.1 N HCl was passed through a 1 ml anion exchange column (5 mm I.D.). The column, which retains both Ag and Pd, was washed with 5 ml 0.1 N HCl and 5 ml 0.001 N HCl. Ag and Pd were eluted successively with 5 ml 9 N HCl and 25 ml 9 N HCl, respectively. The Pd fraction of selected samples which had been totally spiked with ^{102}Pd was then taken for mass spectrometric analysis. The eluate containing the Ag was loaded in 2 ml 0.1 N HCl onto a second anion exchange column (0.16 ml), washed with 2 ml 0.1 N HCl and 1 ml 0.001 N HCl, and eluted with 1 ml 9 N HCl. Subsequently Ag was transferred in 1 ml 0.1 N HNO_3 to a 0.12 ml cation exchange column, washed with 1 ml 0.1 N HNO_3 and 1 ml 0.001 N HCl, and eluted with 2 ml 0.1 N HCl. The cation exchange step was repeated on a second column. Finally Ag was loaded in 2 ml 0.1 N HCl onto a 0.06 ml anion exchange column and washed successively with 2 ml 0.1 N HCl, 5 ml 1N HCl, 1 ml 0.001 N HCl, and 0.2 ml H_2O. The upper part of the column had been carefully cleaned from residual HCl before Ag was eluted with 1.1 ml 1N HNO_3. To the eluate of the last column 2-3 μl 0.1 N H_3PO_4 were added and the solution evaporated to a droplet of ~ 0.1 mm size. Two drops of HNO_3 were added and evaporated. The sample was finally taken up in 8 μl H_2O, added to ~ 0.1 mg silica-gel, which had been previously loaded into a V-shaped Re-filament and dried. The blank for the total chemical and loading procedure was 1.3-2.5x10^{10} atoms of ^{109}Ag. For samples less than 400 mg, the first anion column was omitted

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Table 1. Ag Isotopic Ratio and Concentrations (C) before (I) and after (II) Correction for Blank for Different Fractions (FR) and Central Pieces (CP).

Sample	Metal	$^{107}Ag/^{109}Ag$		C[10^{11} Atoms/g metal]		
				^{109}Ag		$^{107}Ag^*$
	[g]	I[e]	II[f]	I	II	calc.[d]
PIÑON						
#D	3.039					
FR 1	0.774	1.100±0.004	1.100±0.004	(250)	(250)	–
FR 2	0.492	1.150±0.006	1.15±0.01	(50)	(50)	–
CP	1.773	1.64±0.03	1.75±0.06	4.7	3.8±0.2[g]	2.5
#2B	5.531					
CP	2.435	2.10±0.04	2.46±0.19	2.8	2.1±0.2[g]	2.9
#147.A.1	10.835					
CP	5.320	2.65±0.03	2.82±0.05	(1.6)	(1.4)	2.4
SANTA CLARA						
#1060.1	12.063					
FR 2[a]	0.838	1.087±0.001	1.087±0.001	(900)	(900)	–
FR 3	0.842	1.103±0.004	1.103±0.004	(90)	(90)	–
FR 4	0.797	1.22±0.01	1.23±0.01	(8.7)	(8.2)	1.2
FR 5	2.106	1.64±0.02	1.76±0.05	2.9	2.4±0.2[g]	1.6
FR 6	1.896	1.62±0.04	1.77±0.05	(2.4)	(1.9)	1.3
CP	5.535	1.68±0.01	1.76±0.02[h]	2.1	1.9±0.1[g,h]	1.3
#9	5.577					
CP	3.378	1.66±0.02	1.73±0.06	2.8	2.3±0.3[g]	1.5
TLACOTEPEC						
#3	2.485	1.082±0.006[i]	1.082±0.006[i]	28	28±0.8	<0.3
		1.086±0.003[i]	1.086±0.003[i]			
TERRESTRIAL STANDARDS		electron multiplier[e]	Faraday cup[e]			
NBS 978[b]		1.089±0.005	1.083±0.008	–	–	–
Ventron[c]		1.091±0.004	1.080±0.004	–	–	–

[a]The first fraction contained only 49 mg metal and was not analyzed. [b]National Bureau of Standards, Washington, Ag isotopic standard, SRM 978. [c]Ventron Co., Beverly, Mass., Silver shot 99.9999%, Lot 050875. [d]Calculated from columns 4 and 6. [e]Errors: mass spectrometric analysis, 2σ of distribution. [f]Errors: as in [e]) plus scattering of total chemistry blank, 3σ of distribution. [g]Concentration determined by spiking aliquot prior to chemical separation, see [f]) for errors. [h]Isotopic composition and concentration (determined on aliquots of approx. equal size) represent best values for Santa Clara. [i]Detector: Faraday cup.
( ) Concentrations determined on aliquots of composition experiment. Small part spiked after separation assuming yield is 100%.
Data in column 3 are the raw ratios measured at 1000-1040°C (no corrections for $CaPO_2^+$, AsS^+ were necessary). Corrections for blank in this table depend on the size of the aliquots passed through chemistry.

reducing the procedural blank to 5-20x10^9 ^{109}Ag atoms. After each experiment, the resin was discarded and the columns reloaded. After every sample ~ 6x10^{10} atoms ^{109}Ag tracer were passed through the procedure to determine the blank. After every spiked sample a Ag normal of the usual sample size was processed and its isotopic ratio determined to be normal within 0.2-1% establishing that no ^{109}Ag tracer remained.

Mass spectrometry. The thermal ionization mass spectrometer systems used to determine the isotopic ratios were described in detail by *Wasserburg, Papanastassiou, Nenow, and Bauman* [1969]. The technique of measuring Ag was described by KTW and KW. An electron multiplier (gain of ~ 3000) was used as a detector in the current mode for most analyses. The linearity of the multiplier was determined by *Chen and Wasserburg* [1980] for U normals using a $^{233}U/^{236}U$ double spike and was found to be better than 0.5% for currents of 10^4-10^6 ions/sec. Comparison of the performance of the multiplier and the Faraday cup in the same experiment showed that the differences in the measured isotopic ratios of Ag could be explained well within error by the square root of the mass correction law. The smallest ion beams used for isotopic measurements were 10^4-10^6 ions/sec with an ionization efficiency of ~ 1%. The measurements were made at filament temperatures from 1000°C-1250°C to check for possible interferences. The compounds AsS^+ and $CaPO_2^+$, which interfere at mass 107, were monitored at masses 108 and 103, respectively. For all runs at temperatures up to 1100°C no variations in the Ag isotopic composition could be detected other than those due to mass fractionation. At temperatures higher than 1100°C, good agreement with the data taken under normal operating conditions could be obtained after substantial corrections for $CaPO_2^+$ had been applied. An analog scan is shown in Fig. 1. Using slit widths for the source and the detector of 0.1 mm and 0.45 mm, respectively, satellite peaks at masses 105, 106, 107, 108, and 109 due to hydrocarbons could be resolved. With proper focussing and by aid of a coldfinger the intensity of satellite peaks relative to the main peak could be kept at a level which excluded significant contributions to the main peak from the tail of the hydrocarbon peak.

Results. Table 1 shows the results of our Ag analyses. Next to the list of samples, the weight of the meteoritic metal is given for the total sample prior to etching and the weight of each fraction removed for the corresponding analysis. Each solution was divided into aliquots for concentration and composition experiments. The concentrations of Ag are given as the number of ^{109}Ag atoms per gram of dissolved metal in each etching step (columns 5 and 6). We found high ^{109}Ag concentrations in the outermost 100-300 μm thick metal layers of Piñon (#D, 1st fraction) and of Santa Clara (#1060.1, 2nd fraction). With increasing distance from the original surface, the concentration of ^{109}Ag dropped by 2-3 orders of magnitude. The isotopic composition of Ag (rows 3 and 4) close to the surface of the samples was nearly indistinguishable from the terrestrial value. With increasing depth successively higher ratios of $^{107}Ag/^{109}Ag$ were observed but the concentration of $^{107}Ag^*$ remained constant. In the case of Santa Clara #1060.1 there is sufficient data to show that $^{107}Ag/^{109}Ag$ increases as a function of depth and then reaches a constant value for the last three interior samples. The $^{107}Ag/^{109}Ag$ value at this plateau is interpreted as the ratio intrinsic to this piece of the meteorite. The chemical yield of the separation procedure was 70-100% except for two cases where an aliquot was lost. Concentrations given in parentheses in Table 1 were determined by spiking a small part of the eluate with ^{109}Ag tracer after it had been passed unspiked through the chemical procedure. Yields of 100% were assumed. The remainder of the eluate was used to determine the isotopic composition. These concentrations are possibly too small by up to 30%. For the central pieces of Piñon #D, Piñon #2B, Santa Clara #1060.1, and Santa Clara #9, and for fraction 5 of Santa Clara #1060.1 separate aliquots were used to determine the concentration and isotopic composition, the aliquot for the concentration experiment having been spiked with ^{109}Ag tracer before passing it through the chemical procedure. In these cases the corresponding isotopic composition, determined independently (Table 1, col. 3), was introduced into the spike equation. As a correction for the procedural blank and the chemical yield could not be performed independently, a chemical yield of 100% was

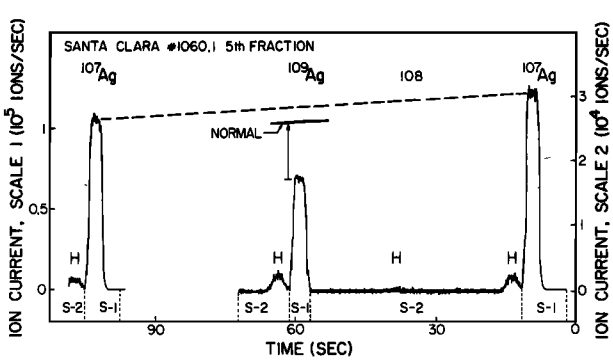

Fig. 1. Analog display of a scan in the Ag mass region, real time vs. ion current (detector: electron multiplier, R = $10^9\Omega$, gain ~ 3x10^3). The decay of the ion beam (dashed line) is monitored by a second scan over mass 107. The "normal" line indicates where the signal of ^{109}Ag in a normal sample would be for the observed ^{107}Ag signal. (H): Small hydrocarbon peaks. S-1 and S-2 refer to scales 1 and 2, respectively. (Sample size: 1.6x10^{11} atoms of ^{109}Ag.)

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Table 2. Ag-Pd Isotopic Ratios in Central Pieces

	$^{107}Ag/^{108}Pd$	$^{107}Ag^*/^{108}Pd$	$^{109}Ag/^{110}Pd$
Piñon #D	$3.3x10^{-5}$	$1.3x10^{-5}$	$4.3x10^{-5}$
Piñon #2B	$2.6x10^{-5}$	$1.5x10^{-5}$	$2.4x10^{-5}$
Santa Clara #1060.1	$2.3x10^{-5}$	$0.9x10^{-5}$	$2.9x10^{-5}$
Santa Clara #9	$2.7x10^{-5}$	$1.0x10^{-5}$	$3.5x10^{-5}$

assumed. This might have introduced an error of up to 20% into the calculation in addition to the error of the concentration data given in Table 1, col. 6. Our results strongly indicate a contamination of the sample surfaces with terrestrial Ag which could be removed by dissolving a metal layer of 0.5-1 mm from the surface. The contamination was detectable as deep as 0.5 mm below the surface indicating material containing Ag had been worked into the metal during sawing. The level of ^{109}Ag found in the cleaned samples (central pieces in Table 1) is smaller by 1-2 orders of magnitude than the smallest Ag concentration for any iron meteorite ever reported. It is possible that some earlier determinations of Ag as well as other minor trace elements in iron meteorites may have been affected by this kind of problem. The contamination is not manifest at the high concentration levels of Pd. The Pd concentrations were determined on aliquots of the solutions of the central pieces for Piñon #D and #2B, and for Santa Clara #9 and #1060.1. The results were 13.2±0.2 μg/g and 13.0±0.2 μg/g for the Piñon samples and 9.8±0.2 μg/g and 9.7±0.1 μg/g for the Santa Clara samples. These agree within 2% with the Pd concentrations reported by KW. The constant Pd concentrations indicate that there was no differential dissolution of phases enriched in Pd and support the argument that the "etching" procedures simply dissolved the bulk layer of the meteorite samples. The $^{107}Ag/^{108}Pd$, $^{107}Ag^*/^{108}Pd$, and $^{109}Ag/^{110}Pd$ ratios for selected samples are shown in Table 2. The concentrations of $^{107}Ag^*$ and Pd reported earlier by KW are fully confirmed by this work.

In addition to the data on Santa Clara and Piñon presented above, we also report on the Ag isotopic composition in Tlacotepec, a IVB iron meteorite (Table 1). The concentrations of Ag and Pd were given by KW2 (Pd/Ag = 6370) and the isotopic composition was reported orally [KW2]. However, the sample surface had not been thoroughly cleaned by etching. As a result the Ag concentration obtained may be too high and correspondingly the $^{107}Ag/^{109}Ag$ ratio too small due to a contamination with normal Ag. Nevertheless, it may be safely concluded from these data that $^{107}Ag^* < 0.3x10^{11}$ atoms/g and $^{107}Ag^*/^{108}Pd < 3x10^{-6}$ in Tlacotepec.

Discussion

The silver contents of Piñon and Santa Clara were found to be extremely low and of highly unusual isotopic composition. The concentration level of 1-4 x 10^{11} ^{109}Ag atoms/g is much smaller than that reported by KW and is less by 1-2 orders of magnitude than all Ag concentrations so far measured in meteorites. The $^{107}Ag/^{109}Ag$ ratio is found to range from 1.7 to 2.8 as compared with the measured normal value of 1.09. This corresponds to a relative increase in $^{107}Ag/^{109}Ag$ of 60-160% compared to normal Ag and is approximately 10 times higher than that reported earlier by KW. The number of atoms of excess $^{107}Ag^*/g$ meteorite, assuming the ^{109}Ag represents normal Ag, is different for these two meteorites and identical to the values reported by KW. The present results show that the correlation of $^{107}Ag/^{109}Ag$ and Pd/Ag reported earlier for Santa Clara [KW2] was a result of terrestrial Ag contamination of the sample surfaces. Anomalous Ag has so far been found only in meteorites which have a very high Pd/Ag ratio. While the anomalous Ag observed in the Santa Clara and Piñon iron meteorites is reasonably well explained by the presence of normal solar system Ag and $^{107}Ag^*$ from *in situ* decay of ^{107}Pd, it is important to consider alternative possibilities such as irradiation of the meteorite parent body or *in situ* fission of a siderophilic or chalcophilic superheavy element. In the following we will discuss each of these possible mechanisms.

Late stage nucleosynthesis. The production of ^{107}Pd along with ^{26}Al and some ^{129}I is a plausible explanation of the presence of $^{107}Ag^*$ in meteorites with high ratios of Pd/Ag. This appears quantitatively compatible with the observed abundances of $^{107}Ag^*/^{108}Pd$ and the short ^{26}Al time scale implied by the correlation of $^{26}Mg^*$ with ^{27}Al [*Lee, Papanastassiou and Wasserburg*, 1977]. This matter was extensively discussed by KW who pointed out that the presence of ^{107}Pd of nucleosynthetic origin in iron meteorites would provide a direct temporal connection between a sudden late nucleosynthetic event and the formation and differentiation of small planets. So far ^{26}Al and ^{107}Pd are the only two nuclei with half lives less than 10^7 yr for which positive evidence exists, although a small negative anomaly in ^{135}Ba in the Cl FUN inclusion suggests condensation occured before complete decay of ^{135}Cs ($\tau_{1/2}$ = $2.3x10^6$y) [*McCulloch and Wasserburg*, 1978]. Isotopic analysis of coexisting phases in iron meteorites are required to demonstrate a correlation between $^{107}Ag/^{109}Ag$ with $Pd/^{109}Ag$. In a system such as Piñon, which has $^{110}Pd/^{109}Ag = 2.3x10^4$ and an inferred initial $(^{107}Pd/^{110}Pd)_0 = 3x10^{-5}$, assuming the initial $(^{107}Ag/^{109}Ag)_0$ was normal, the $^{107}Ag/^{109}Ag$ growth curve is changing initially at the rate of $6\%/10^6$y. In principle, it may be possible to resolve differences as small as $\sim 10^5$y if a low Pd/Ag phase, such as troilite, can be analyzed.

Irradiation. The possibility of an intense local proton irradiation in the early solar system has been most recently discussed by *Lee* [1978]. Effects from long term bombardment by galactic cosmic rays can be excluded as a source for isotopic anomalies in stony meteorites both in terms of general nuclear systematics and the short irradiation ages of these bodies. For some iron meteorites with long irradiation ages, it is possible that some isotopic effects may be due to nuclear reactions. In particular, Ag isotopes produced by the bombardment of Pd in iron meteorites could yield a data array which is almost indistinguishable from that resulting from *in situ* decay of ^{107}Pd produced in late stage nucleosynthesis. There is at present no cosmic ray irradiation age of Santa Clara. For Piñon a very old exposure age of ~ 1 AE has been estimated from the $^3He/^4He$ ratios [*Bauer*, 1963] and from the isotopic composition of K [*Voshage*, 1967; *Voshage and Feldman*, 1979]. The concentrations of ^4He, ^{21}Ne, and the excesses of ^{33}S and ^{36}S due to spallation on Fe in Piñon were determined to be $3.8x10^{14}$, $1.3x10^{12}$, $4x10^{11}$, and $1x10^{11}$ atoms/g, respectively [*Bauer*, 1963; *Voshage*, 1967; *Hulston and Thode*, 1965]. These values are commensurate with the number of Ag atoms in Piñon. However, the target Pd is 10^6 times less abundant than Fe. Monte Carlo calculations for interaction of 1 and 3 GeV protons with an iron target showed that depending on irradiation geometry, mainly due to secondary neutrons, products with masses close to the target mass can be produced several orders of magnitude more efficiently than products like Ne from Fe [*Armstrong*, 1969]. Inspection of Table 2 shows that $^{107}Ag^*/^{108}Pd \sim 10^{-5}$ and $^{109}Ag/^{110}Pd \sim 3x10^{-5}$. If for simplicity we assume that the ^{107}Ag and ^{109}Ag result from nuclear interactions on ^{108}Pd and ^{110}Pd, respectively, it follows that $\sigma\phi\tau \sim 10^{-5}$. Taking the cosmic ray irradiation age (τ) of Piñon to be 1 AE we obtain $\sigma\phi \sim 3x10^{-22}$ sec^{-1}, where σ may be written as $\sum_R \langle \sigma_R(E)\, M_R(E) \rangle \sim 10^2$ barn, assuming a constant integral primary cosmic ray flux (ϕ) of 3 protons cm^{-2}sec^{-1}. Here brackets $\langle\rangle$ denote averaging over the energy E of the interacting particles; σ_R is the cross section for the reaction R in units of barn. The multiplicity, M_R, is defined as $\phi_R(E)\,\phi^{-1}$, where ϕ_R is the differential flux of interacting particles for reaction R. If the irradiation age were 4.5 AE, then this would give $\sum_R \langle \sigma_R M_R \rangle \sim 20$ barn. It is possible that the effective cross section and multiplicity are high enough in zones of an iron meteorite so that major contributions to both Ag isotopes might occur. If there were no normal solar system Ag in the meteorite, the abundance of $^{107}Ag/^{109}Ag$ would be a direct reflection of the target abundances and $\sum_R \langle \sigma_R M_R \rangle$. If $\sum_R \langle \sigma_R M_R \rangle$ were the same for ^{108}Pd and ^{110}Pd, we would expect $(^{107}Ag/^{109}Ag) \sim (^{108}Pd/^{110}Pd) \sim 2.3$. This is close to the values found in Piñon but quite different from the value in Santa Clara. From these considerations, it is seen that cosmic ray effects may be significant. However, the meteorite Tlacotepec has $^{107}Ag^*/^{108}Pd < 3x10^{-6}$ even though it has a cosmic ray exposure age comparable to that of Piñon. The concentrations of ^4He and ^{21}Ne in Tlacotepec are also somewhat larger than those in Piñon [*Voshage*, 1967]. These observations indicate that either the flux of lower energy interacting particles was much less in Tlacotepec than in Piñon or that the $^{107}Ag^*$ in Piñon was not produced by cosmic rays. If it were possible to find $^{107}Ag^*$ in an iron meteorite with a very young exposure age, then the arguments in favor of ^{107}Pd from nucleosynthetic sources would be greatly strengthened. A more extensive analysis of the nuclear interactions on Pd in iron meteorites is clearly required.

Fission. It was noted earlier by KW that fission of a transuranic or superheavy siderophilic element could produce $^{107}Ag^*$. The present $^{107}Ag/^{109}Ag$ could also conceivably be produced by fission. The concentration of the hypothetical progenitor would be 2-20 x 10^{13} atoms/g assuming a 1-0.1% fission yield. *Libby, Libby, and Runcorn* [1979] have speculated that the more abundant trace elements in iron meteorites might be the result of *in situ* fission. In particular, they suggest that an elemental abundance peak near $Z \sim 43$ observed in iron meteorites represents a SHE fission peak. Accordingly, unshielded isotopes of Pd and Ag should have comparable abundances and should exhibit a highly fissionogenic pattern. However, the Pd isotopic composition in Santa Clara has been shown to be identical to terrestrial Pd to 0.05% [KW1]. We believe that almost all of the existing elemental abundances in iron meteorites stand in contradiction to their point of view and that the observations on Ag place more realistic constraints on a fission source.

Chemical abundances of Ag. Piñon and Santa Clara are closely related to the IVB iron meteorites which show a general trend of being depleted in volatile elements and enriched in refractory, siderophilic elements. This is considered to indicate that the parent body of the IVB iron meteorites consisted of high temperature condensates, condensation being the dominant fractionation mechanism for the volatile siderophilic elements [*Scott,* 1972; *Kelly and Larimer,* 1977; *Sears,* 1978]. The Ag concentration in the first FeNi metal grains condensed in equilibrium from a cooling nebula of solar composition can be estimated. Assuming the solid AgFeNi metal phase to be ideal, the concentration of ^{109}Ag should be $2x10^{11}$ atoms/g at 1275°K and 10^{-5} bars. If account is taken of the very low solubility of Ag in γ-Fe [*Wriedt, Morrison, and Cole,* 1973] to estimate the activity coefficient of Ag, an upper limit for the Ag concentration is obtained which lies 2 or more orders of magnitudes lower than the ^{109}Ag concentrations found in Piñon and Santa Clara for a temperature and pressure in the solar nebula as high as 1500 K and 10^{-2} atm. The observed atomic ratio of $^{109}Ag/Ni$ in these meteorites is 10^{-10} which is a factor of $\sim 10^4$ lower than the solar value of 4.5 x 10^{-6}. The observed depletion factor provides additional support for arguments that Piñon and Santa Clara are products of condensation and accretion of metal grains at high temperature which were subsequently agglomerated to form part of a small parent planet which then melted to form these meteorites. The fraction of low temperature material present in the parent body must have been very small in order to preserve the characteristic depletion pattern in volatile siderophilic elements. It is conceivable that the parent planet consisted almost entirely of metal, olivine and high temperature Ca-Al rich minerals. From the above estimates of the concentration of Ag in a solid FeNi phase, which was in equilibrium with a nebular gas at high temperature, it is seen that the values are far below those observed in Piñon and Santa Clara. This raises the possibility that some FeNi meteorites were formed with virtually no solar Ag. If this consideration were to apply to Santa Clara and Piñon, it would then be necessary to explain both the observed ^{109}Ag and the ^{107}Ag in these bodies as a result of nucleosynthetic or cosmic ray bombardment processes.

Conclusions

Ag concentrations found in Piñon and Santa Clara are 1-4 x 10^{11} atoms ^{109}Ag/g meteoritic metal. The isotopic composition of Ag shows large excesses of ^{107}Ag of 60-160% compared to normal Ag. The concentration of $^{107}Ag^*$ atoms and the ratio of $^{107}Ag^*/^{108}Pd \sim 10^{-5}$, which were reported earlier by KW, are fully confirmed. We have shown, however, that the high ^{109}Ag concentration and small relative excesses of ^{107}Ag reported earlier were the result of terrestrial contamination of the sample surfaces. Isotopically anomalous Ag has so far only been found in meteorites with high Pd/Ag ratio. As stated earlier, *in situ* decay of ^{107}Pd ($\tau_{1/2}$ = 6.5x10^6y) is a plausible source of $^{107}Ag^*$. This inference has important consequences for the time scale for condensation and early planetary differentiation in the solar system. There is as yet insufficient evidence to conclusively prove that ^{107}Pd existed in the early solar system as a result of the injection of freshly synthesized nuclear material just before the solar system formed. Possible contributions from the interaction of galactic cosmic rays on Pd will have to be investigated to clarify this matter.

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References

Armstrong, T.W., Monte Carlo calculations of residual nuclei production in thick iron targets bombarded by 1- and 3-GeV protons and comparison with experiment, *J. Geophys. Res.,74,* 1361-1373, 1969.

Bauer, C.A., The helium contents of metallic meteorites, *J. Geophys. Res.,68,* 6043-6057, 1963.

Buchwald, V.F., Handbook of iron meteorites, University of California Press, Berkeley, vol. 3,pp. 978-981, 1975.

Chen, J., and G.J. Wasserburg, A search for isotopic anomalies in uranium, *Geophys. Res. Lett.,* this issue.

Hulston, J.R., and H.G. Thode, Cosmic-ray-produced ^{36}S and ^{33}S in the metallic phase of iron meteorites, *J. Geophys. Res.,70,* 4435-4442, 1965.

Kelly, W.R., and J.W. Larimer, Chemical fractionations in meteorites -VIII. Iron meteorites and the cosmochemical history of the metal phase, *Geochim. Cosmochim. Acta, 41,* 93-111, 1977.

Kelly, W.R., F. Tera, and G.J. Wasserburg, Isotopic determination of Ag in picomole quantities by surface ionization mass spectrometry, *Anal. Chem.,50,* 1279-1286, 1978.

Kelly, W.R., and G.J. Wasserburg, Evidence for the existence of ^{107}Pd in the early solar system, *Geophys. Res. Lett.,5,* 1079-1082, 1978.

Kelly, W.R., and G.J. Wasserburg, Evidence of ^{107}Pd in the early solar system, X. Lunar and Planetary Science Conf., Abstracts, vol. 2, pp. 652-654, The Lunar and Planetary Institute, Houston, Texas, 1979.

Lee, T., A local proton irradiation model for isotopic anomalies in the solar system, *Ap. J.,224,* 217-226, 1978.

Lee, T., D.A. Papanastassiou, and G.J. Wasserburg, ^{26}Al in the early solar system: Fossil or Fuel?, *Ap. J.* (Letters), *211,* L107-L110, 1977.

Libby, L.M., W.F. Libby, and S.K. Runcorn, The possibility of superheavy elements in iron meteorites, *Nature, 278,* 613-617, 1979.

McCulloch, M.T., and G.J. Wasserburg, Ba and Nd isotopic anomalies in the Allende meteorite, *Ap. J.,220,* L15-L19, 1978.

Sanz, H.G., and G.J. Wasserburg, Determination of an internal ^{87}Rb-^{87}Sr isochron for the Olivenza chondrite, *Earth and Planet. Sci. Lett.,6,* 335-345, 1969.

Scott, E.R.D., Chemical fractionation in iron meteorites and its interpretation, *Geochim. Cosmochim. Acta, 36,* 1205-1236, 1972.

Sears, D.W., Condensation and the composition of iron meteorites, *Earth and Planet. Sci. Lett.,41,* 128-138, 1978.

Tera, F., and G.J. Wasserburg, Precise isotopic analysis of Pb in picomole and subpicomole quantities, *Anal. Chem.,47,* 2214-2220, 1975.

Voshage, H., Bestrahlungsalter und Herkunft der Eisenmeteorite, *Z. Naturforsch.,22a,* 477-506, 1967.

Voshage, H., and H. Feldmann, Investigations on cosmic-ray-produced nuclides in iron meteorites, *Earth and Planet, Sci. Lett.,45,* 293-308, 1979.

Wasserburg, G.J., D.A. Papanastassiou, E.V. Nenow, and C.A. Bauman, A programmable magnetic field mass spectrometer with on-line data processing, *Rev. Sci. Instr.,40,* 288-295, 1969.

Wriedt, H.A., W.B. Morrison, and W.E. Cole, The solubility of silver in γ-Fe, *Metallurg. Trans.,4,* 1453-1456, 1973.

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